

Band-structure and core-hole effects in resonant inelastic soft-x-ray scattering: Experiment and Theory

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INTRODUCTION

Resonant soft-x-ray fluorescence spectroscopy (RSXF) refers to the study of the changes in x-ray emission spectra as the excitation energy is varied near a core-level absorption threshold. It has been the application of RSXF to solids in the soft-x-ray regime that has garnered most of the interest in the past decade [1]. Although the description of the scattering in terms of purely delocalized states [2, 3, 4, 5] is appealing in its simplicity, serious questions have arisen concerning the validity of this picture [6, 7]. In core-level absorption spectroscopy (XAS or NEXAFS), core-hole effects and core excitons are clearly observed, and have long been known to dramatically affect the interpretation of absorption spectra [8]. Since the final states in XAS are the intermediate states in RSXF, it has been argued that an interpretation which omits excitonic effects is intrinsically suspect [6]. In fact, it has been asserted in at least one work that the inclusion of such effects is necessary in order to correctly account for the experimental data [7].

In this work, we will focus on the possible role core-hole effects have on the RIXS in a particular system: graphite. This will be accomplished by examining, at higher resolution than previously attainable, the changes in the scattering near the σ^* and π^* absorption thresholds in this material. Comparisons will then be made to simulated spectra that include or exclude core-hole effects. Our conclusion is that core-excitons have only minor effects on the emission features, even though they clearly have a pronounced effect on the total fluorescence yield. However, other spectral features are not fully accounted for by the inclusion of core excitons in the scattering.

RESULTS AND DISCUSSION

Due to recent advances in the storage ring at the ALS, Beamline 8.0 now delivers, by more than an order of magnitude, more flux in the 100-1000 eV range ($\approx 1.3 \times 10^{13}$ photons/sec for $\Delta h\nu \approx 60$ meV). This affords us the opportunity to examine, with much higher resolution than in previous studies, the crystal momentum conservation and selectivity during RIXS, for intermediate state energies near well-known core-excitons, while retaining data acquisition times around ten minutes. This can be accomplished by narrowing the bandwidth of the excitation energy $\Delta h\nu$ down to ≈ 60 meV. This reduction of the bandwidth narrows the widths of the iso-energy contours in the BZ that are summed over during the RIXS process (i.e. the spread of crystal momenta in the BZ is reduced). Figures 1 & 2 show RSXF data collected near the π^* (Fig. 1) & σ^* (Fig. 2) absorption edges in graphite, using both narrow- and wide-band excitation ($\Delta h\nu \approx 60$ meV or 500 meV).

Through comparison of Fig. 1(A) and 1(B), it is clear that narrow-band excitation has a marked effect on the measured spectra. Features in Fig. 1(B) are sharper than in Fig. 1(A). As the excitation energy increases, the transition from emission around the K point ($h\nu' \approx 272$ eV) to emission around M ($h\nu' \approx 276$ eV) occurs over a narrower range of excitation energies. Note carefully the upper π -band emission ($h\nu' = 281$ – 283 eV) in Fig. 1(A) versus Fig. 1(B). Whereas in Fig. 1(A) there is a range of energies for which emissions from both the K and M branches of the upper π bands are observed simultaneously, reduction of the excitation bandwidth leads to a much more smooth transition in Fig 1(B).

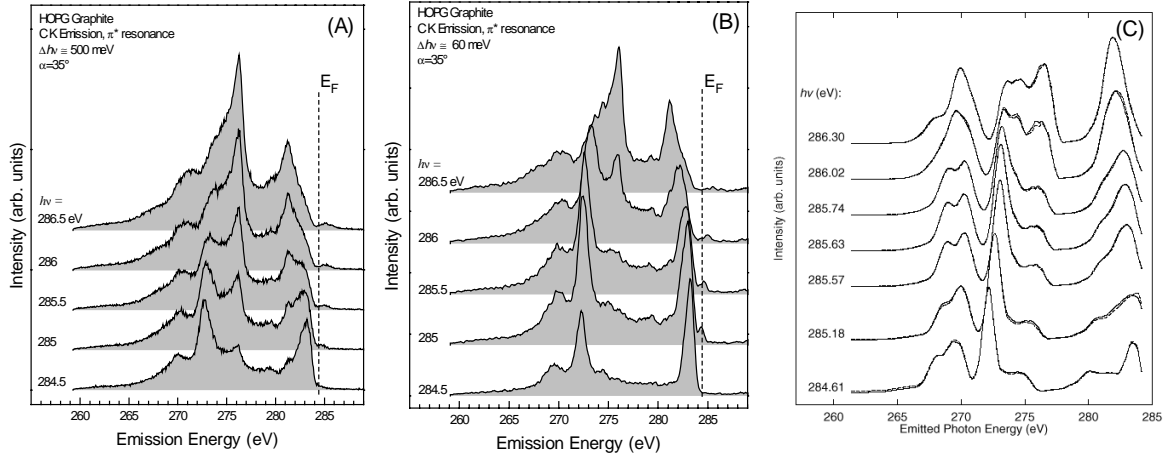


Fig. 1. (A,B) Experimental RIXS spectra for HOPG collected for excitation energies near the π^* absorption threshold of 284.5 eV, but using different excitation energy bandwidths ($\Delta h\nu$). The excitation energies are given to the left of each spectrum. The width of the incident radiation for these spectra is approximately (A) $\Delta h\nu \approx 300$ meV and (B) 60 meV. Note the abrupt onset of emission at $h\nu' = 276$ eV. (C) Simulated RIXS in graphite near the π^* threshold. Solid lines correspond to simulated spectra obtained with core-hole effects included, whereas dashed lines are spectra obtained without inclusion of these effects.

Simulated emission spectra for excitation energies near the π^* threshold, generated with (solid lines) and without (dashed lines) the inclusion of core-hole effects, are shown in Fig. 1(C). Note that the dashed and solid curves nearly overlap each other, and that the agreement between theory and experiment is very good throughout the range of energies near the π^* threshold. Clearly, momentum conservation and selectivity are very much in force for all the excitation energies above, equal to, and below the π^* energy. In fact, careful comparison with the simulated spectra in Fig. 1(C) shows that using the narrower bandwidth enhances the agreement between theory and experiment in the K-to-M transition region.

The apparent absence of core-hole effects can be qualitatively explained as follows. Core-hole effects are strong in XAS since the core-hole is present the final state. However, in RIXS, the core-hole is present only in an intermediate state. Although the corresponding exciton can be more localized in real space, and thus more delocalized in momentum space, the final momenta which participate in the scattering are determined by the projection of the excitonic state onto the RIXS final state, which contains an electron in the conduction band and a hole in the valence band. These final states are almost certainly not as localized as the core excitonic states. Thus, momentum selectivity is for the most part the same as one would expect based on a one-electron or non-interaction picture.

The above explanation is sensible for excitons whose binding energies lie within the continuum of conduction band states, as for the π^* exciton above. However, at the σ^* edge, there is a well known exciton that is well-separated from the bottom of the σ^* bands near the M-point in the graphite band structure, with a binding energy estimated to be 0.1 to 0.2 eV [4, 9]. Fig. 2(A) shows RSXF spectra obtained near the σ^* absorption edge using $\Delta h\nu \cong 500$ meV, and Fig. 2(B) show similar spectra obtained using $\Delta h\nu \cong 60$ meV. As opposed to data acquired near the π^* edge, the spectra obtained using the narrower bandwidth have several addition features, highlighted by the dotted line and arrows in Fig. 2(B). The feature located at $h\nu' \cong 281$ eV does not move with excitation energy, and is detectable over a narrow energy range (~ 0.5 eV). Note that its appearance and disappearance corresponds exactly with the σ^* absorption energy ($h\nu \cong \sim 291.6$ eV). Two other, weaker, features also rise and fall with the appearance of the 281 eV feature, located at roughly 276 eV and 269 eV.

Inspection of the graphite band structure indicates that these features are derived from states at the M-point in the BZ. Apparently, in this range of excitation energies \mathbf{k} -selectivity is present to a significant degree, and the portion of the BZ selected is near M. This data strongly suggests that a highly localized intermediate state exists near the bottom of the σ^* bands at M, and that this state slightly influences the scattering for a narrow range of energies centered on the M-point.

Note carefully that these emission features do not move in energy as the excitation energy is varied. In a non-interacting picture, we would observe an M-to- Γ cross-over, similar to the K-to-M cross-over discussed above. For instance, we should observe a very rapid dispersion, to lower emission energy, of the 281 eV feature, as $h\nu$ varies from roughly 291 eV to 292.5 eV. The fact that they do not move suggests that a highly localized, excitonic state (comprised of a narrow range of \mathbf{k} -values near M) dominates the RIXS in this narrow intermediate state energy range.

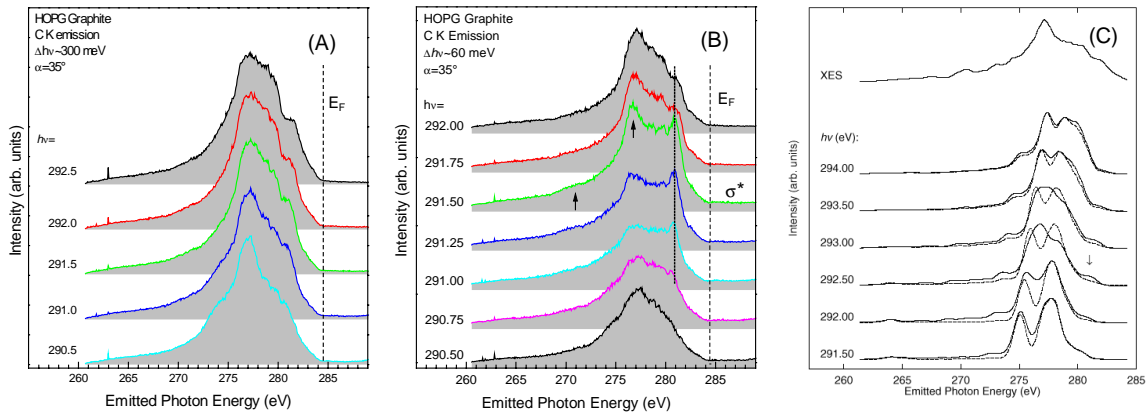


Fig. 2. (A,B) Experimental RIXS spectra for HOPG collected for excitation energies near the σ^* absorption threshold of 291.6 eV, but using different excitation energy bandwidths ($\Delta h\nu$). The excitation energies are given to the left of each spectrum. The emission near 281 eV (dotted line) is consistent with final states corresponding to a $\pi \rightarrow \sigma^*$ promotion near M. This feature does not move with the excitation energy. Note also the absence in (A) of the emission feature at 281 eV and at other energies highlighted by the arrows in (A). (C) Simulated RIXS in graphite near the σ^* threshold. There are significant differences between the simulations, and that the agreement between theory and experiment is improved via the inclusion of core-hole effects.

The assignment of these features to excitonic effects is further supported by the simulated spectra shown in Fig. 2(C). RIXS spectra have been generated for excitation energies corresponding to the σ^* exciton region, with the solid and dashed lines representing spectra obtained with and without excitonic effects as before. As opposed to Fig. 1(C), there are now clear qualitative differences between the dashed and solid curves. Note too that the agreement between theory and experiment is improved by the inclusion of core-hole effects. Thus, based on the experiments and the comparison with simulated spectra generated without core-hole effects, we conclude that excitons have only minor effects on the detailed line-shape of the resonant emission spectra in graphite. This conclusion can be extended to a number of other systems [1].

SUMMARY

To summarize, we have demonstrated that the RIXS present in resonant fluorescence spectra above a core-level absorption threshold may be utilized to probe the band structure of a material, as first put forward by Ma [2]. We have probed, using narrow-band excitation, the role core-hole effects play in the RIXS process. In graphite, core-hole effects result in only minor changes to the resonant emission spectra. The ability of RIXS to examine the \mathbf{k} -resolved electronic structure, coupled with the intrinsic strengths of soft-x-ray fluorescence for probing the bulk-sensitive and element-resolved electronic structure of materials, demonstrates the great potential of this technique for probing the electronic structure of novel materials systems which are often inaccessible to other techniques.

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